

REMARKS

The Telephone Interview:

The Examiner is thanked for discussing the rejections with the undersigned on the telephone on November 30, 2005. The Examiner indicated the arguments set forth herein appeared to be persuasive but did not commit himself to withdrawal of the rejections without further study.

The Amendments:

The specification has been amended to correct the priority claim. Support for the amendment is found on the Inventors' Declaration filed with this application.

Claims 40-43 have been cancelled without prejudice. Applicants reserve the right to present such claims in a divisional or continuing application.

New claim 44 has been added to specify that the process is a continuous process in which at least a portion of the resin is regenerated and returned to the process. Support is found, e.g. in the second full paragraph of page 4, and the first and second full paragraphs.

The Objection to the Disclosure:

The Disclosure has been objected to because the specification fails to contain a reference to prior U.S. Application Serial. No. 10/650,785, to which priority is apparently claimed in view of this application having been listed on the Information Disclosure Statement filed April 6, 2005. The priority claim was incorrectly listed on the Information Disclosure Statement. The undersigned apologizes for any confusion this may have caused. It is not necessary to claim priority to Serial. No. 10/650,786 because Application 08/809,044, to which the present application claims priority, was still pending as of the filing date hereof, November 17, 2003. Application No. 08/809,044 issued as Patent No. 6,669,849 December 30, 2003.

The Obviousness-type Double Patenting Rejections:

The claims are provisionally rejected for obviousness-type double patenting over the claims of Application Serial. No. 10/640,785 and Patent No. 6,669,849. Terminal Disclaimers are submitted herewith to overcome these rejections.

The Rejection under Section 112, First Paragraph:

Claims 42 and 43 are rejected as not supported by the specification. This rejection is obviated by cancellation of these claims. Please note, however, that the claims have been cancelled without prejudice. Applicants do not concur that this is a valid rejection and reserve the right to present these claims in a continuing or divisional application.

The Rejection under Section 102:

Claims 42 and 43 have been rejected as anticipated by Patent Application Publication No. 2002/0121479, since the Examiner alleges they are not entitled to the priority date claimed herein. Again, these claims have been cancelled without prejudice. Applicants do not concur that this is a valid rejection and reserve the right to present these claims in a continuing or divisional application.

The Rejection under Section 103 over Jowett et al. in view of Weiss et al.

Claims 1-6, 8, 10-17, 19, 20, 22-33 and 35-40 have been rejected under Section 103a) as obvious over Jowett et al. (Patent No. 4,154,675) in view of Weiss et al. (Patent No. 3,560,378). The Office Action states:

Jowett et al. discloses removing organic carbon from water by dispersing an ion-exchange resin into the water, separating the resin from the resultant mixture, and regenerating the resin with brine for reuse (see col. 11, lines 57-60; and col. 12, lines 13-15). This reference further discloses that the water can be subjected to additional treatments of the type recited (see col. 7, lines 42-44; and col. 8, lines 28-30). Accordingly, Jowett et al. discloses the claimed invention with the exception of the use of magnetic ion-exchange resin particles. Weiss et al. discloses magnetic ion-exchange resin particles of the type recited; and it would have been

obvious to one of ordinary skill in the art at the time the invention was made to substitute the magnetic ion-exchange resin particles of the secondary reference for the ion-exchange resin particles of the primary reference, in order to enable separation of the resin from the treated water by magnetic means.

This rejection is respectfully traversed. Jowett et al. discloses using a cellulosic ion-exchange material. that is at most about 10% cross-linked (Abstract; col. 4, lines 6-7) to adsorb protein, fat and carbohydrate materials (col. 3, lines 45-56) from streams such as egg white, milk, or liquid extract or waste effluent such as soya whey, milk whey or extracts from various seeds and nuts, or blood (col. 3, lines 57-65). The patent mentions that the process can be used for "purification of water for domestic use" (col. 4, lines 2-3), but does not provide any specific enablement for this use. The cellulose has a large dry particle size (40-100 mesh (col. 6, lines 1-2) and during use it swells even more to form a mechanically weak porous structure (col. 2, lines 39-45).

The Weiss et al. patent discloses magnetic ion-exchange resins that are more highly cross-linked than those described in Jowett et al., e.g., polyethylenime and polyacrylic acid resins (see, e.g., Example 3). The beads of this resin are produced in such a way as to wholly encapsulate the ferromagnetic particles that make them magnetic (col. 2, lines 14-22; col. 8, lines 1-2). The patent discloses that these resins are capable of adsorbing inorganic compounds. The patent does not teach or suggest that the resin is capable of adsorbing dissolved organic compounds.

The Office Action asserts that it would be obvious to substitute the magnetic ion-exchange resin of Weiss et al. for the cellulosic material of Jowett et al. "in order to enable separation of the resin from the treated water by magnetic means."

However no *prima facie* case of obviousness has been made out because Jowett et al. teaches against such a combination and there is no motivation for

combining the disclosures of these two patents. Jowett et al.'s purpose is to separate fats, proteins and carbohydrates from liquids and Jowett et al.'s process uses an ion-exchange agent known to be useful for this purpose, namely a cellulosic ion-exchange material (col. 1, lines 15-26). It would not be obvious to one skilled in the art to substitute the more highly crosslinked magnetic ion-exchange resin of Weiss et al. into the Jowett et al. process, because Jowett et al. teaches that its material is not more than 10% crosslinked. Thus, Jowett et al. teaches against the use of the more highly crosslinked magnetic ion-exchange resin of Weiss et al. It is well-settled that a reference (in this case Jowett, et al.) that teaches against a particular element (in this case a highly crosslinked resin as described in Weiss) cannot be combined with that element in order to formulate an obviousness rejection. It is well settled that a reference that teaches against a claimed invention may not be used to formulate an obviousness rejection. (See, e.g., *Mitsubishi Elec. Corp. v. Ampex Corp.* 190 F.3d 1300, 51 U.S.P.Q.2d 1910 (CAFC 1999))

Further, the Jowett et al. disclosure describes a *process* developed specifically for use with swellable non- or low-crosslinked cellulosic ion-exchange material. This swellable material is said to avoid the reduction in ion-exchange capacity which results from crosslinking, thereby maximizing capacity for polyelectrolytes and other large ions (column 4, lines 10-15). The swellable nature of the Jowett, et al. materials due to the lack of or low crosslinking would make them unsuited to packing in ion-exchange columns, and accordingly, it was necessary for Jowett et al. to develop an alternate means for contacting the liquid medium with the swellable material they had developed. Accordingly, it would not have been obvious to substitute a small, more highly crosslinked magnetic ion-exchange resin for the large swellable non- or low-crosslinked material for which the Jowett process was specifically developed. The Jowett et al. reference therefore provides no motivation for using a more highly crosslinked resin in its process, as one skilled in the art, from a reading of the reference, would not see a need for a more highly crosslinked resin.

Furthermore, no *prima facie* obviousness rejection has been made out because Weiss et al. does not teach or suggest that the magnetic resin used in its process is useful for adsorbing proteins, carbohydrates and fats, or indeed any organic compound. It would therefore not be obvious to one skilled in the art to utilize the magnetic resin of Weiss et al. to remove fats, carbohydrates and proteins from fluids, which is the purpose of the Jowett et al. reference. There is therefore no motivation within the references to combine them. The Office Action offers ease of separation of the magnetic resin from the treated water as a possible motivation for combining the references, but this is not relevant when the purpose of making the combination (separation of fats, carbohydrates and proteins) is not known by those of skill in the art to be possible using the substitution.

It is submitted that one skilled in the art would not read Jowett et al. as a process for treating water for domestic use unless the impurities intended to be removed were the fats, carbohydrates and/or proteins referred to in the reference, because, as stated in the Background section of Jowett et al., that is what its cellulosic ion-exchange agents are known for. As set forth in Section 1.3 of the "Water Quality" Section of the Government of British Columbia's website (copy attached as Exhibit A) the concentration of proteins, carbohydrates and fats in water is usually low, and most of the DOCs in water are humic substances. If simpler, humic dissolved organic carbons are present, Jowett et al. teaches that these are removed in a polisher or deodorizer (item 13 of Figure 2, col. 9, lines 39-41) containing activated carbon or a catalytic system. Thus, if the fluid to be treated contained only simple, humic DOC, and not fats, carbohydrates and proteins, one skilled in the art would understand from Jowett et al. that only activated carbon or a catalytic system for removing DOC would be required, and that ion-exchange agents would not be required. Furthermore, one skilled in the art would not look to Jowett et al., a process for removing fats, carbohydrates and proteins from materials like milk, if his goal was to purify water, since water primarily contains humic DOCs rather than fats, carbohydrates

and proteins. Thus there would be no motivation to combine the Jowett et al. process with Weiss, et al.

It is therefore submitted that the claims are not obvious in view of the references, and withdrawal of the rejection is respectfully requested.

In the telephone interview of November 30, 1005, the Examiner mentioned that it might be considered obvious to incorporate the ferromagnetic particles of Weiss et al. into the cellulosic ion exchange material of Jowett et al. to arrive at a combination that would render the present claims obvious.

However, one skilled in the art would not be motivated to make such a combination to treat water for removal of DOC as claimed herein because, as shown in Exhibit A, water contains very little of the fats, proteins and carbohydrates removed by the Jowett et al. process, and thus the Jowett et al. reference would not be considered relevant to DOC removal from water, and there would be no motivation to use it by itself, or combined with the ferromagnetic particles of Weiss et al. for water treatment. Thus, in the absence of motivation to combine the references, no *prima facie* case of obviousness is made out.

Further there is no enablement in the references for making cellulosic ion exchange materials incorporating ferromagnetic particles. The Jowett et al. reference teaches that cellulosic material is a "mechanically weak, porous structure" (Col. 2, line 45), and it is submitted that such a material would not be likely to retain the ferromagnetic particles of Weiss et al.

The cellulosic ion exchange material of Jowett et al. is described as being that of U.S. Patent No. 3,905,954 (copy enclosed as Exhibit B). The process for preparing this ion exchange material involves a number of steps including final steps of dissolving the material in caustic soda and reprecipitating it (col. 3, lines 1-25 of Exhibit B). It is not clear how one would go about incorporating

ferromagnetic particles into the ion exchange material of Jowett et al. using such a process. It is not clear how ferromagnetic particles could be caused to precipitate as part of the precipitated product, especially as Weiss et al. teaches it is important that the ferromagnetic particles be completely encapsulated within the ion exchange material to prevent abrasion of the particles (col. 2, second full paragraph). In the event the ferromagnetic particles could somehow be incorporated into the precipitated cellulosic ion exchange material, it appears very unlikely that they could be completely encapsulated therein.

It is submitted that the references provide no motivation for combining their disclosures as suggested by the Examiner to incorporate ferromagnetic particles of Weiss et al. into the cellulosic ion exchange material of Jowett et al. Therefore, no *prima facie* case of obviousness has been made out. In addition, the references do not enable such a combination, and therefore cannot be properly cited in an obviousness rejection.

The Rejection under Section 103 over Jowett et al. in view of Weiss et al. in further view of Carlson, et al.

Claims 7 and 18 have been rejected as obvious over Jowett et al. and Weiss et al. as applied above, and further in view of Carlson et al. (U.S. Patent No. 4,670,154). The Office Action states:

The modified primary reference discloses the claimed invention with the exception of the recited vacuum collection step. Carlson et al. teaches (col. 3, lines 19-22) that it is known to transfer ion-exchange resins utilizing a vacuum generating device. It would have been obvious to one of ordinary skill in the art at the time the invention was made to transfer the resin of the modified primary reference in the manner taught by Carlson et al., in order to obtain the advantages disclosed by this secondary reference for the system of the modified primary reference.

It is submitted that the Carlson et al. reference does not supply the deficiencies of the primary references, namely, it does not provide motivation for combining the primary references, nor does it teach removing dissolved organic carbon

using a magnetic ion-exchange resin. Thus, it does not render the independent claims obvious, and for that reason, dependent claims 7 and 18 are also not obvious over the cited references. Further, one skilled in the art would not find it obvious to utilize the venturi-type vacuum device disclosed in Carlson et al. for drawing a non-magnetic ion-exchange resin into a flow line in order to collect a magnetic resin which has agglomerated, as the physical properties of a magnetically agglomerated magnetic resin are likely to be different from those of a non-magnetic resin. Withdrawal of this rejection is thus respectfully requested.

The Rejection under Section 103 over Jowett et al. in view of Weiss et al. in further view of Corne et al.

Claims 9 and 21 have been rejected as obvious over Jowett et al. and Weiss et al. as applied above, and further in view of Corne et al. (U.S. Patent No. 1,190,863). The Office Action states:

The modified primary reference discloses the claimed invention with the exception of the recited tilted plates. Come et al. discloses (see Fig. 9) a settling tank having a series of tilted plates. It would have been obvious to one of ordinary skill in the art at the time the invention was made to substitute the settling tank of the secondary reference for the settler of the modified primary reference (see col. 8, line 30 of Jowett et al.), since this secondary reference settling tank is capable of separating solids from a liquid in substantially the same manner as the settler of the modified primary reference, to produce substantially the same results.

It is submitted that the Corne et al. reference does not supply the deficiencies of the primary references, namely, it does not provide motivation for combining the primary references, nor does it teach removing dissolved organic carbon using a magnetic ion-exchange resin. Thus, it does not render the independent claims obvious, and for that reason, dependent claims 9 and 21 are also not obvious over the cited references. Moreover, the Corne et al. settling tanks are used for settling mud, scale, and fine particles of bagasse from cane juice in the manufacture of sugar, not for separating magnetic resin particles. It would not be obvious to one skilled in the art that such settling plates would operate well to

recover magnetic ion-exchange resin beads as in the present process, in view of the different physical properties of the muds and particles found in sugar cane juice from those of magnetic ion-exchange resins. Withdrawal of this rejection is thus respectfully requested.

The Rejection under Section 103 over Jowett et al. in view of Weiss et al. in further view of Bacchus et al.

Claims 34 and 41 have been rejected as obvious over Jowett et al. and Weiss et al. as applied above, and further in view of Bacchus et al. (U.S. Patent No. 6,110,375). The Office Action states:

The modified primary reference discloses the claimed invention with the exception of the recited membrane treatment. Bacchus et al. teaches purifying water with an ion-exchange resin, and subsequently subjecting the water to a treatment by a membrane filter (see col. 2, lines 50-60). It would have been obvious to one of ordinary skill in the art at the time the invention was made to subject the ion-exchange resin treated water of the modified primary reference to a membrane filtration treatment, as suggested by Bacchus et al., in order to further purify this water.

It is submitted that the Bacchus et al. reference does not supply the deficiencies of the primary references, namely, it does not provide motivation for combining the primary references, nor does it teach removing dissolved organic carbon using a magnetic ion-exchange resin. Thus, it does not render the independent claims obvious, and for that reason, dependent claims 34 and 41 are also not obvious over the cited references. Moreover, it is unlikely one of skill in the art would think it useful to combine Bacchus et al. with Jowett et al. in view of the fact that Jowett et al. discloses that post-treatments after treatment with the cellulosic ion-exchange agent include chlorination, dissolved gas removal, removal of organic materials by an activated carbon or a catalytic system, and oxidation or further ion-exchange treatment (col. 7, lines 41-50). No mention of the use of membrane filtration is disclosed, presumably because the post-ion-exchange fluid of Jowett et al. is not sufficiently pure to be subjected to

membrane filtration without immediately fouling the membrane. Withdrawal of this rejection is thus respectfully requested.

The Rejection under Section 103 over Jowett et al. in view of Bacchus et al.

Claims 42 and 43 have been rejected as obvious over Jowett et al. in view of Bacchus et al. (U.S. Patent No. 6,110,375). This rejection has been obviated by cancellation of claims 42 and 43; however, it is pointed out that these claims have been cancelled without prejudice. Applicants do not concur that this rejection is proper and reserve the right to re-present claims 42 and 43 in a divisional or continuing application.

Conclusion

In view of the foregoing, it is submitted that this case is in condition for allowance, and passage to issuance is respectfully requested.

If there are any outstanding issues related to patentability, the courtesy of a telephone interview is requested, and the Examiner is invited to call to arrange a mutually convenient time.

It is believed that this response necessitates the payment of \$260 for two Terminal Disclaimers. A check in this amount is enclosed. Also enclosed is a Statement Under 27 CFR 3.73(b). If this is incorrect, however, please charge any fees due or for any extension of time required to Deposit Account No. 07-1969.

Application No. 10/716,198
Amendment dated December 1, 2005
Response to Office Action of September 1, 2005

Respectfully submitted,



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AMENDMENT
EXHIBIT A

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• Government of British Columbia

Water, Air and Climate Change Branch**Ministry of
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WATER QUALITY

Definitions, Concepts and Analytical Measurements

1.1 Key Concepts

Organic matter in aquatic systems is a complex mixture of molecules such as carbohydrates, amino acids, hydrocarbons, fatty acids and phenolics, natural macromolecules and colloids (e.g., humics), sewage and industrial particulates, soil organic matter, living phytoplankton and other plant material. These materials are of interest for several reasons. Their transport contributes significantly to the global carbon cycle. For example, the transport of soil-derived organic matter by rivers and its subsequent burial in marine sediments is an important global sink for carbon. The more reactive constituents of organic matter (e.g., carbohydrates) make a significant contribution to heterotrophic metabolism in streams, lakes, estuaries and coastal areas. Fulvic acids and other humic substances affect the behaviour and transport of metals by complexing them. These compounds also interact with organic pollutants and adsorb to the surfaces of mineral solids thus affecting surface chemistry and rates of aggregation.

Most waters contain organic matter that can be measured as total organic carbon (TOC). Sources of organic carbon in fresh and marine waters include living material and waste materials and effluents. Organic matter from living material may arise directly from plant photosynthesis or indirectly from terrestrial organic matter. An indication of the amount of organic matter present can be obtained by measuring related properties, principally the biochemical oxygen demand (BOD), chemical oxygen demand (COD), turbidity and colour. The COD usually includes the BOD as well as other chemical demands producing the relationship, COD greater than BOD greater than TOC. If the sample contains toxic substances, however, this relationship may not hold true. Turbidity is a function of light scattering by suspended particles, while colour is related to the quantity of dissolved (true colour) and particulate substances (apparent colour) present. As a result, both parameters are often highly correlated with organic carbon levels.

The total organic carbon in water can be a useful indication of the degree of pollution, particularly when concentrations can be compared upstream and downstream of potential sources of pollution. In surface waters, total organic carbon concentrations are generally less than 10 mg/L, and in ground water less than 2 mg/L, unless the water receives wastes or is highly coloured due to natural organic material (e.g., swamps, bogs). Total organic carbon consists of dissolved (DOC) and particulate organic carbon (POC) and is therefore affected by pronounced fluctuations in suspended solids in riverine systems. The DOC and POC levels are determined separately after filtering the sample through a filter approximately 0.4 to 0.7 micron pore diameter. Typically, DOC levels exceed POC levels in the range 6:1 to 10:1, except during river floods or in highly turbid waters where POC dominates (Wetzel 1975).

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1.2 Particulate Organic Carbon

The particulate organic carbon fraction of total organic carbon has three major sources:

allochthonous inputs from the drainage basin (e.g., leaf litter), and autochthonous inputs from the littoral and pelagic zones of carbon flux. Much of the metabolism and decomposition of particulate organic carbon takes place in the sediments or en route during sedimentation. The characteristics and rates of transport of organic carbon from the drainage basin depend on the composition of soils and parent materials, local climatic conditions, topography, hydrology, and vegetation of the watershed (Mitchell and McDonald 1995; Håkanson 1993; Heikkinen 1994; Midgley and Schafer 1992). In addition, some land use activities (e.g., animal husbandry) tend to accelerate soil erosion, thereby increasing the potential for problematic levels of particulate and total organic carbon in the water column, while other activities (e.g., clear cutting) tend to decrease organic carbon inputs (Shields and Sanders 1986; Forsberg 1992; France 1995a,b).

1.3 Dissolved Organic Carbon

Dissolved organic carbon is composed primarily of two categories of substances: (i) non-humic substances, a class of compounds that includes carbohydrates, proteins, peptides, fats, pigments and other low molecular weight compounds, and (ii) humic substances which form most of the organic matter in waters, and consist of coloured hydrophilic and acidic complexes ranging in molecular weight from the hundreds to thousands (Wetzel 1975). Non-humic substances are easily utilized and degraded by microorganisms (i.e., substances are labile) and exhibit rapid flux rates in aquatic systems. Their instantaneous concentrations are usually very low as a result, although they may play an important role in system metabolism. Humic substances are formed largely as a result of microbial activity on plant and animal material and are more persistent than non-humic substances.

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1.4 Analytical Methods

Total organic carbon (TOC) is determined without filtration of the sample. Samples for TOC determination should be stored in dark glass bottles, with minimum exposure to light or air, at 3 to 4 C for no more than seven days prior to analysis. Alternatively, samples can be acidified with nitric, phosphoric or sulphuric acid to pH 3 or less for longer term storage and to eliminate inorganic carbon. Samples for DOC determination follow a protocol similar to that for TOC, except that they are filtered (pore diameter = 0.4 to 0.7 micron, 0.45 micron being the most common) to remove particulate organic carbon.

There are several methods available for determining organic carbon depending on the type of sample to be analyzed. Methods are based on the principle of oxidation of the carbon in the sample to carbon dioxide (e.g., combustion, chemical reaction, ultraviolet radiation) which is then determined by one of several methods (e.g., volumetric determination, thermal conductivity, specific CO₂ electrode). The US EPA (1983) describes these methods in detail. Wet oxidation methods (e.g., UV persulphate) have been shown to underestimate total combustion techniques by 15 to 30 percent, most likely because of incomplete oxidation of organic carbon to CO₂ (Clair 1992).

Several specialized techniques are available to characterize the different forms of organic matter in water and wastewaters. For example, Thomas et al. (1993) and Huber and Frimmel (1992, 1994) describe a technique that involves separating out the organic matter fractions by molecular weight and other physical chemical properties using 3D low pressure gel chromatography, and characterizing the chromatographic fractions with high sensitivity DOC and UV detection. The detection limit for chromatographic techniques is in the range of several milligrams per liter and thus a pre-concentration step is necessary. Chromatographic techniques can be used to determine, for example, the fraction of humics that make up the DOC in the sample.

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BC Environment (Water, Land and Air Protection) measures total organic carbon by converting it to CO₂ via catalytic combustion or wet chemical oxidation, and then measuring the CO₂ formed by infrared detector or converted to methane and measured by flame ionization (BC Environment 1994). Based on the findings of Clair (1992), the catalytic combustion technique is preferable to the wet chemical oxidation technique. The detection limit for TOC in drinking, surface, and waste waters is 1 mg/L. All samples are stored in cool (4 degrees Celcius), dark conditions in sealed containers. As with other jurisdictions, un-preserved samples must be analyzed within 72 hours. Preserved samples (i.e., pH adjusted to less than 2) must be analyzed within 28 days. Environment Canada (1995) uses a somewhat different approach to determining TOC and DOC levels in water. The analysis is comprised of two phases, the determination of total carbon or dissolved carbon and the determination of total inorganic carbon or dissolved inorganic carbon. TOC and DOC levels are then determined by difference. To do this, each sample is split into two. Total and dissolve carbon are determined by combusting the one split sample in the presence of a platinum catalyst at an elevated temperature with an oxygen gas carrier. Total and dissolved organic carbon are determined in the other split sample by combustion in a phosphoric acid solution through which the carrier gas is bubbled. An infrared detector is used to determine the CO₂ formed. The normal detection limit is 0.5 mg/L. Note that with this methodology, sample preservation by acidification to pH less than 2 is not recommended because it will result in the partial loss of the inorganic components.

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AMENDMENT
EXHIBIT B**United States Patent** [19]

Jones et al.

[11] 3,905,954

[45] Sept. 16, 1975

[54] **ACTIVATED CELLULOSE**[75] Inventors: **David Thomas Jones**, Ystalysera;
Kenneth Rowland Rees, Dunvant;
George Edward Jowett, Uplands, all
of Wales[73] Assignee: **Viscose Development Company**
Limited, Croydon, England[22] Filed: **July 21, 1972**[21] Appl. No.: **273,766**[30] **Foreign Application Priority Data**

July 23, 1971 United Kingdom..... 34645/71

[52] U.S. Cl. 260/212; 106/122; 210/500;
252/176; 260/218; 264/191; 264/195; 264/196[51] Int. Cl.² C08B 15/00; C08L 1/24[58] Field of Search 264/191, 192, 194, 195,
264/196, 197; 106/122; 260/218, 212[56] **References Cited****UNITED STATES PATENTS**1,936,479 11/1933 Koch..... 264/192
2,021,864 11/1935 Lilienfeld..... 264/192
2,125,031 7/1938 Polak et al..... 260/2182,860,480 11/1958 Cox..... 264/194
3,068,545 12/1962 Stiner..... 106/122
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3,501,419 3/1970 Bridgeford..... 106/168
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3,591,667 7/1971 Kulshrestha 264/218**FOREIGN PATENTS OR APPLICATIONS**368,288 2/1932 United Kingdom..... 260/212
390,519 4/1933 United Kingdom..... 260/212
459,124 12/1936 United Kingdom..... 260/212
546,493 9/1956 Belgium..... 260/212
981,362 1/1965 United Kingdom..... 260/212*Primary Examiner*—Ronald W. Griffin*Attorney, Agent, or Firm*—Brisebois & Kruger[57] **ABSTRACT**

Ion exchange activated cellulose in the form of porous bodies, caps, tubes, beads, granules or powders is prepared by reacting unregenerated cellulose with a compound having ionizable chemical groups which impart ion exchange properties to the cellulose reaction product and then regenerating said product.

11 Claims, No Drawings

ACTIVATED CELLULOSE

This invention relates to activated cellulose and, more especially, to cellulose ion-exchange materials.

An ion-exchange material in general consists of an inert substrate into which are introduced ionizable chemical groups which are normally basic or acidic in nature and capable of binding anions or cations, respectively, by a process analogous to salt formation. Such bound ions may be exchanged for different ions when the chemical environment of the material is changed.

Ion-exchange materials based on cellulose substrates have been prepared by combining a suitable compound containing an ionizable chemical group with natural or regenerated cellulose. The hitherto proposed materials are, however, costly because of their expensive preparation and have other disadvantages.

A particular disadvantage of the hitherto proposed ion exchange materials based on natural or regenerated cellulose is their limited exchange capacity for relatively large ions, for example, ions derived from proteins or carbohydrates. Further, the previously proposed materials based on regenerated cellulose can be prepared satisfactorily in only a few physical forms. Thus, for example, difficulties arise in preparing an ion exchange material from cellulose that has been regenerated in the form of a sponge. The activating conditions tend to bring about a degradation of the sponge structure and produce an irregular pore size distribution and a tendency towards physical instability. Also, combination between the activating substance and the regenerated cellulose is mainly restricted to the cellulose surface. Similar difficulties arise in activating regenerated cellulose in other physical forms, for example, films.

The fibrous character of natural cellulose also imposes physical limitations, and restricts the range of applications for which ion exchange materials based thereon can be employed and renders such materials unsuitable, for example, for the extraction of proteins from waste effluents.

The present invention provides a process for the preparation of an ion exchange activated regenerated cellulose wherein a substance which combines with cellulose and contains an ion exchange active component is incorporated before the final regeneration of the cellulose.

The process of the invention enables ion exchange activated regenerated celluloses to be obtained in a wide variety of physical forms, including many that have hitherto been difficult or impossible to attain. Further, the activated regenerated cellulose is generally obtained relatively economically and has superior absorption and/or ion exchange properties for large ions. Examples of large ions for which the ion exchange activated regenerated cellulose will generally be found suitable include ions derived from proteins such as enzymes and components of blood and tissue; carbohydrates, for example, charged polysaccharides such as the mucopolysaccharides; nucleic acids, for example, ribonucleic acids and deoxyribonucleic acids; dye-stuffs, for example, Congo Red; fatty acids, and quaternary ammonium compounds.

The present invention is especially directed to the preparation of ion-exchange activated cellulose and the active component is therefore preferably an ionizable chemical group as discussed hereinbefore. Suitable

substances which may be associated with cellulose to form ion-exchange materials are well known in the art. There may be mentioned, for example, compounds containing amino, alkylamino, guanidino and quaternary amino groups for the preparation of anion-exchange materials, e.g. diethylamino ethyl chloride, di(hydroxyethyl)amino ethyl chloride, dimethylamino ethyl chloride, 1-(diethylamino)-2,3-epoxy propanol, p-morpholino ethyl chloride and salts thereof; and compounds containing sulpho, phosphoric and carboxyl groups for cation-exchange materials, e.g. chloromethane sulphonic acid, chloroethane sulphonic acid and 1,3-propane sultone.

Compounds are also known which can be attached to cellulose to form materials capable of fixing biologically active materials such as, for example, enzymes. (see, for example, British Patent No. 1,183,259), and the use of such compounds is also included within the scope of the present invention. Thus, for example, the activating substance may be a compound containing pendant triazinyl groups. Preferably, in addition to such an activating substance, an activating substance is used in which the active component is an ionizable chemical group.

It will in most cases be preferable to cross-link the cellulose to some extent so as to obtain extra structural stability. Any of the cross-linking agents known in the art may be used for this purpose including, for example, epichlorhydrin, dichlorhydrin, dibromoethane, dichloroethane, 1,2,3,4-diepoxybutane, bisepoxy propyl ether, ethylene glycol bisepoxy propyl ether and 1,4-butanediol bisepoxy propyl ether. The above-mentioned cross-linking agents are generally employed in alkaline solution, e.g. aqueous sodium hydroxide. It is also possible to use other chemical cross-linking agents such as aldehydes, e.g. formaldehyde, which are employed in acidic solution. Alternatively, cross-linking may be achieved physically by using ionising radiation such as ultra-violet radiation, gamma rays or electron beams, optionally in the presence of sensitizing chemicals. Cross-linking may be effected either simultaneously with the incorporation of the activating substances, in which case the activating substances should of course not interfere with cross-linking (or vice-versa), or may be carried out at another stage in the regeneration process. It will in some cases be advantageous to effect the cross-linking even after the cellulose has been regenerated.

The properties of the finished product will depend to some extent on the degree of cross-linking utilised, and the degree of cross-linking can be controlled in accordance with the final properties required. In general, however, the degree of cross-linking will be from 0.1 to 10%, especially from 1 to 10%, expressed in terms of the weight of cross-linking agent and the dry weight of the regenerated cellulose, although up to 30% may be required in order to obtain special properties. It will be appreciated that the degree of cross-linking selected in any given case will depend on the degree of substitution and degree of solubility of the cellulose material.

The present invention is especially applicable to the viscose process for the preparation of regenerated cellulose and in an especially preferred embodiment of the present invention a regenerated cellulose is prepared by the following steps:

1. Preparation of alkali cellulose. This can be achieved by any suitable method including the traditional one of soaking sheets of wood pulp in caustic soda, pressing out surplus caustic soda, and disintegrating the sheets to form crumbs of alkali cellulose. Instead, the alkali cellulose may be prepared by grinding natural cellulose to a powder and impregnating the powder with a limited quantity of caustic soda solution.
2. Treat with an ion-exchange activating substance, for example, diethylchloromethylamine hydrochloride, and with a cross-linking agent such as epichlorhydrin.
3. Treat with caustic soda.
4. Treat with carbon disulphide.
5. Dissolve the product in a solution of caustic soda.
6. Precipitate in the required form by a known regeneration method, for example, by the action of heat; by means of an acid; by treatment with a hot strong electrolyte; or by treatment with a strong electrolyte followed by an acid. One or more reinforcing agents and/or poreforming materials may be added prior to regeneration. Examples of reinforcing agents include hemp, flax, cotton, viscose yarn, nylon and polyester. As pore-forming materials there may be mentioned sodium sulphate and sodium phosphate.

The activating substance and/or the cross-linking agent can be incorporated at other stages prior to regeneration, or the cross-linking agent may be incorporated after regeneration. Mixtures of two or more activating substances and/or cross-linking agents can be employed if desired.

The activated regenerated cellulose may be prepared in any of a wide variety of forms as may be required. Examples of such forms include a spongy porous body, a rigid or semi-rigid porous body, a film, a sheet, a cap, a filament, a tube or a rod (of any desired section) or a particulate form such as beads, granules or a powder.

Furthermore, the cellulose may, if required, be regenerated into or onto a support comprising an inert material such as, for example, a rigid porous mass of a ceramic material. In this way, a considerable variety of physical forms can be obtained, for example, packing for columns. Instead, after regeneration, the cellulose may be incorporated into a matrix or support, which is preferably formed of an inert material, so as to obtain special forms or structures. For example, an activated regenerated cellulose in particulate form may be incorporated into a porous bag or container made of an inert material, or into a cartridge formed of inert material and having porous end walls.

The present invention is also applicable to the preparation of regenerated cellulose by methods other than the viscose process, for example, the cuprammonium and acid regeneration process.

Ion-exchange materials prepared according to the process of the present invention have the ability to absorb larger ions than has generally heretofore been the case, and have relatively high exchange capacities for large ions. Accordingly, the materials can be used for a widely differing range of ions. Further, the ion-exchange material is dimensionally stable, especially if partially cross-linked, and is relatively resistant to disintegration. The present invention accordingly also provides an ion-exchanger which includes an ionexchange material prepared according to the above process.

It is a feature of materials prepared according to the process of the present invention that, because the activating substance is well dispersed within the cellulose solution when regeneration takes place, it becomes distributed uniformly throughout the precipitated cellulose, as distinct from being concentrated mainly at the surfaces of the cellulose.

It will be appreciated that optimum ion-exchange capacity, for large molecules is not compatible with a high degree of rigidity produced by extensive cross-linking, since the cross-linking reduces the extent to which the activating substance is accessible for exchange purposes.

The activated regenerated cellulose has properties which produce advantages in fields other than ion-exchange, and the present invention is therefore not to be construed as limited to the use of the regenerated cellulose only for ion-exchange methods. For example, the activated material may be used as an anti-clotting agent when dialysing blood.

Whilst the present invention is especially applicable to the preparation of activated regenerated cellulose, it may also be used for the preparation of activated regenerated cellulose derivatives, for example, methyl cellulose, ethyl cellulose, hydroxyethyl cellulose, ethylhydroxy ethyl cellulose and allyl cellulose.

The quantity of activating substance incorporated with the cellulose may be from 20 to 80% by weight (based on the dry weight of the cellulose).

The following Examples illustrate the invention:

EXAMPLE 1

Natural cellulose in the form of the steeping-grade pulp normally supplied to the Viscose industry was steeped in 18% (w/v) caustic soda solution, and the steeped pulp was drained and then pressed to a press ratio of 3.3. The resulting alkali cellulose, which comprised 27.5% cellulose, 15.5% caustic soda, and 57% water, was shredded in a Z-arm grinder to form crumbs.

363.5 Gm. of the alkali cellulose crumbs were conditioned at 5°C. in a Z-arm mixer, and 58.3 gm. N,N-diethyl 2-chloroethylamine hydrochloride were added to the cool crumbs. The resulting mass was mixed for 30 minutes at 5°C., after which time the temperature was raised to 50°C. and reaction allowed to continue for a further 60 minutes. The temperature was then reduced to 30°C. and 65 gm. carbon disulphide were added to the reacting mass. The ensuing xanthation reaction was allowed to continue for 60 minutes at 30°C., giving a diethylaminoethyl, (DEAE), cellulose xanthate having a γ number of 89. (As will be understood by those skilled in the art, the γ number provides a measure of the degree of substitution of the cellulose by xanthate groups).

An activated regenerated cellulose sponge was produced from the DEAE cellulose xanthate as follows:

153.5 Gm. of 18.8% (w/v) caustic soda and 802 gm. water were added to 651.4 gm. of the xanthate to yield a viscose solution. 51.5 Gm. cotton fibre as reinforcing agent and 5,500 gm. of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (Glauber's Salt) as pore-forming agent were then added to the solution, yielding a paste. The paste was extruded into small cylindrical moulds and was then regenerated in sodium sulphate solution at 95°-100°C., the concentration of Na_2SO_4 being 25% (w/v). The resulting sponge had an

ion exchange capacity (for small ions, for example, Cl^-) of 0.95 meq/gm.

EXAMPLE 2

DEAE cellulose xanthate was prepared as described in Example 1, and a viscose solution was prepared therefrom by treating 651.4 gm. of the xanthate with 385 gm. of 18.8% (w/v) caustic soda solution and 3415 gm. water. The viscose solution was then diluted with water in the ratio of 1 part viscose to 5 parts water. After dilution, the viscose was sprayed by means of compressed air into a regenerating solution comprising 0.5% sulphuric acid and 10% sodium sulphate. The cellulose was thereby regenerated in the form of a fine powder (200-400 mesh B.S.S.) which was washed to remove by-products and was then found to have an ion exchange capacity of 1.13 meq/gm.

EXAMPLE 3

A viscose solution (DEAE cellulose) was prepared as described in Example 2. A film was cast from the solution by weighing 25 gm. of the viscose onto a metal tray 6 inches square and one-fourth inch deep. The viscose was spread over the whole tray and a uniform film thickness was obtained by passing a knife over the surface. After discarding surplus viscose, the film was coagulated by immersing the tray in 30% ammonium sulphate for 20 minutes. The coagulated film was then removed from the tray and immersed for 20 minutes in 12% sulphuric acid to complete the regeneration.

After being washed to remove residual acid and salts, the film was dried and ground and had an ion exchange capacity of 1.09 meq/gm.

EXAMPLE 4

This Example illustrates simultaneous xanthation and activation.

To 1340 gm. of CEPO powdered cellulose SS200 (made by Svenska Tramjol Sfabrikerna) contained in a Z-arm mixer was added a solution of 300 gm. caustic soda and 400 gm. N,N-diethyl 2-chloroethylamine hydrochloride in 1000 gm. water, followed immediately by 650 gm. carbon disulphide. The mass was mixed at 5°C. for 30 minutes, after which time the temperature was raised to 30°C. and the reaction was allowed to continue for a further 90 minutes at that temperature.

The DEAE cellulose xanthate product was made into viscose as described in Example 3, and an ion exchange film was produced from the viscose as described in that Example. The ion exchange capacity of the film, after drying and grinding, was 0.79 meq/gm.

EXAMPLE 5

Carboxymethyl cellulose was prepared by reacting natural cellulose with caustic soda and with chloroacetic acid as activating agent. A clear viscose solution was obtained from the carboxymethyl cellulose by dispersing 100 gm. of the cellulose in 2500 gm. of 17.0% (w/v) caustic soda solution, adding 15 mls. of carbon disulphide, and tumbling the resulting mass for 2½ hours at 25°C.

One portion of the viscose solution was regenerated as described in Example 1 to form a sponge (ion exchange capacity 0.46 meq/gm), and another portion was regenerated as described in Example 3 to form a film (ion exchange capacity 0.59 meq/gm).

EXAMPLE 6

To 134 gm. of CEPO SS200 cellulose powder (Svenska) was added a solution of 50 gm. of N,N-diethyl 2-chloroethylamine hydrochloride, 30 gm. of caustic soda, 0.2 gm. epichlorhydrin and 100 gm. of water. The mass was mixed for 30 minutes at a temperature of 5°C, then raised to a temperature of 50°C for a further 60 minutes, yielding a cross-linked DEAE cellulose.

The reaction mixture was cooled to 30°C., and 65 gm. carbon disulphide were added to initiate xanthation. Xanthation was continued for 60 minutes at 30°C. and the product was then dissolved to give a viscose solution as described in Example 2. Regeneration was then effected as described in that Example to give a fine powder having an ion exchange capacity of 1.14 meq/gm.

EXAMPLE 7

Powdered activated regenerated cellulose was prepared as described in Example 2. Cross-linking of the cellulose was effected by treating 100 gm. of the powder in a Z-arm mixer with a solution of 2.5 gm. epichlorhydrin, 30 gm. caustic soda, and 100 gm. water. The mass was raised to 50°C. for 20 minutes, and was then washed free of by-products to yield a cross-linked regenerated DEAE cellulose having an ion exchange capacity of 1.11 meq/gm.

EXAMPLE 8

10 Gm. of DEAE cellulose produced as described in Example 1 (up to, but not including, xanthation) was dissolved in 100 ml. of commercially available Shirley Cuprammonium solution with stirring. The resulting solution was cast into a film as described in Example 3 and regenerated by treatment with sulphuric acid, yielding an activated regenerated cellulose film having an ion exchange capacity of 1.0 meq/gm.

EXAMPLE 9

A viscose solution (DEAE cellulose) was prepared as described in Example 2, and Hydronyl LA 3032 one-fourth inch porous ceramic spherical beads were saturated with the viscose solution under vacuum. The vacuum was then released, the surplus viscose drained away, and the DEAE cellulose regenerated onto the porous support by treatment with 12.5% sodium sulphate/sulphuric acid solution. The uptake of dry regenerated DEAE cellulose was 28.6% by weight, based on the dry weight of the beads.

The foregoing Examples illustrate, inter alia, the variety of physical forms in which activated regenerated cellulose can be produced in accordance with the invention. In order to demonstrate the other principal advantage of the process according to the present invention, the exchange capacity for large ions of the products certain of the Examples were determined as follows:

Each ion exchanger was "precycled" in known manner. (Precycling refers to the conventional technique of successive absorption/desorption of ions effected at continually increasing pH). After precycling, each exchange material was suspended in 10 volumes of 0.1 M. chloride-tris buffer at pH 8.35, poured into a column (30 cm. \times 1.5 cm.), and washed with 0.01 M chloride-tris buffer at pH 8.35 (approximately one litre of buffer being employed) until the pH and conductivity of the

column eluate were identical with those of the starting buffer.

Sufficient of the ion exchange material (0.5–1.0 gm. dry weight was then stirred with 700–800 mg. of bovine serum albumin in 75 ml. of the same buffer. Small samples (1–3 ml.) were withdrawn at intervals, centrifuged, and the albumin content was estimated spectrophotometrically (280 nm).

The test procedure was carried out on the powder produced in Example 2, on the films produced in Example 3 and 4, and on the cross-linked material produced in Example 7. In order to provide a basis for comparison with the products of the invention, the procedure was repeated using Whatman DE-52 and a sample of the activated (DEAE) natural cellulose produced by the steps described in Example 1 up to, but not including, xanthation. Whatman DE-52 is a mercerised, crystalline, cross-linked natural cellulose.

The results of the investigations are shown in the following Table, from which the superior properties of the products obtained in accordance with the invention is clearly evident.

Ion exchange material	Albumin capacity (mg/gm)
Example 2	928
Example 3	798
Example 4	480
Example 7	366
Whatman DE-52	313
Activated natural cellulose	288

We claim:

1. A process for preparing an ion exchange activated cellulose in the form of porous bodies, caps, tubes, beads, granules or powders, which comprises reacting unregenerated cellulose with a compound having ioniz-

able chemical groups which impart ion exchange properties to the cellulose reaction product, and thereafter regenerating the activated cellulose reaction product to yield an activated regenerated cellulose having ion exchange properties.

2. A process according to claim 1, which includes the step of cross-linking the cellulose to produce additional structural stability in the product.

3. A process according to claim 2, wherein said cross-linking is effected simultaneously with the incorporation of said activating compound with the unregenerated cellulose.

4. A process according to claim 2, wherein said cross-linking is effected after regeneration of the cellulose.

5. A process according to claim 2, wherein the cellulose is cross-linked to the extent of from 0.1 to 10%.

6. A process according to claim 1, which comprises preparing alkali cellulose, reacting the alkali cellulose with said activating compound and with carbon disulphide, dissolving the material so obtained in caustic soda solution and regenerating the resulting viscose to yield an activated regenerated cellulose.

7. A process according to claim 1, wherein a quantity of from 20 to 80% by weight of the ion exchange activating compound based on the dry weight of the unregenerated cellulose is incorporated with said cellulose.

8. A process according to claim 1, wherein regeneration is effected by the action of heat.

9. A process according to claim 1, wherein regeneration is effected by treatment with a strong electrolyte in combination with thermal treatment.

10. A process according to claim 1, wherein regeneration is effected by spraying the cellulosic medium into an acidic regenerating solution.

11. A process according to claim 1, wherein the cellulose is regenerated on a support.

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